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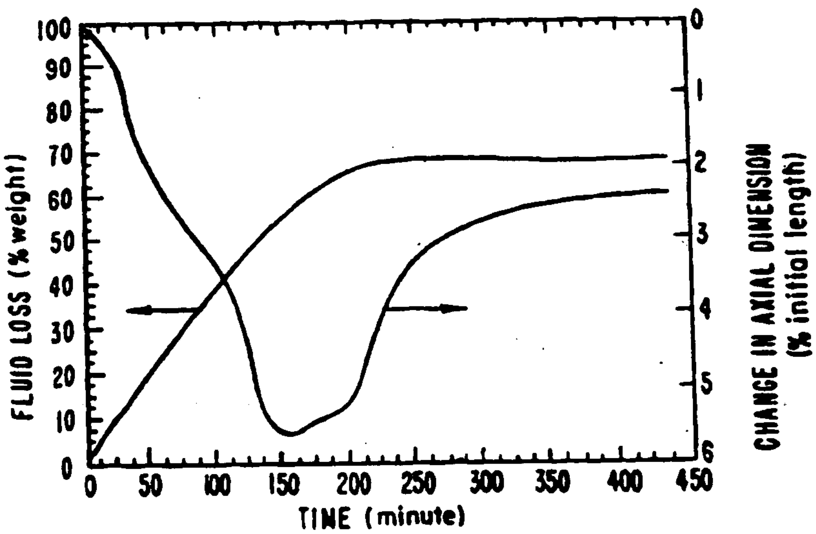

(57) Abstract

This invention provides an extremely porous xerogel dried at vacuum to below-supercritical pressures but having the properties of aerogels which are typically dried at supercritical pressures. This is done by reacting the internal pore surface of the wet gel (e.g. alkoxide-derived silica gel) with an organic surface modification agent (e.g. trimethylchloro-silane in benzene) in order to change the contact angle of the fluid meniscus in the pores during drying. Shrinkage of the gel (which is normally prevented by the use of high autoclave pressures, such that the pore fluid is at temperature and pressure above its critical value) is avoided even at vacuum or ambient pressures. The figure 4 shows a change in sample weight and sample length during drying for surface modified, ambient pressure gel processed in accordance with the invention, illustrating the initial shrinkage followed by expansion of the gel during the final stages of drying. The extremely low density finely pored gel products have useful insulating and other properties.

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PREPARATION OF HIGH POROSITY XEROGELS BY CHEMICAL SURFACE MODIFICATION

Technical Field

This invention is in the field of extremely porous materials such as aerogels and more particularly to aerogels and processes for making aerogels having ultra-fine microstructure and extraordinary properties such as very high insulation qualities. Xerogels are made by the removal of fluid from a fluid-containing gel when the solvent is removed by evaporation and normally exhibit a lower amount of porosity.

Background Art

Aerogels and xerogels are extremely porous materials representing the lower end of the density spectrum of man-made materials. Densities as low as 0.003 g/cm^3 have been reported for silica aerogels (L.W. Hrubesh, Chemistry and Industry, 24 (1990) 824). These fascinating materials have numerous unique properties as a result of their ultra-fine microstructure. Aerogels with the porosities in the range of 0.85 to 0.98 may be transparent and translucent. The porosity is defined as the fraction of the sample volume which is pores. Aerogels exhibit strong Rayleigh scattering in blue region and very weak in red region. In the infrared (IR) region of electromagnetic spectrum, the radiation is strongly attenuated by absorption leading to application in radioactive diode systems, which effectively transmit solar radiation but prevent thermal IR leakage (J. Fricke and R. Caps in Ultrastructure Processing of Advanced Ceramics: Ed. J.D. Mackenzie and D.R. Ulrich, Wiley, New York, 1988). Unusual acoustic properties (sound velocity as low as 100

m/s) suggests use in impedance matching and other acoustic applications. Aerogels with a refractive index of 1.015 to 1.06 cover the region not occupied by any gas or solid resulting in applications in high energy physics.

Silica aerogels with their thermal conductivities as low as 0.02 W/mK (0.01 W/mK when evacuated) find application in superinsulation systems (J. Fricke in Sol-Gel Technology for Thin Films, Fibers, Performs, Electronics and Speciality Shapes: Ed. L.C. Klein, Noyes Publications, Park Ridge NJ, 1988). Fricke has described several aerogel applications based on their insulating properties. They include reduction of heat losses through windows, energy-effective greenhouses, translucent insulation for solar collectors, and solar ponds for long-term energy storage. Fricke has also discussed the mechanism for thermal transport through aerogel tiles and the efforts of density and gas pressure on their thermal conductivity.

Since aerogels are made by sol-gel processing, their microstructure may be tailored to optimize properties desired for specific applications. Various precursors, including metal alkoxides, colloidal suspensions, and a combination of both under several mechanisms of gelation may be used to synthesize gels (C.J. Brinker and G.W. Scherer, Sol-Gel Science, Academic Press, San Diego, 1990). By varying aging conditions such as time, temperature, pH, and pore fluid, the parent wet gel micro-structure may be altered (P.J. Davis, C.J. Brinker and D.M. Smith, Journal of Non-Crystalline Solids; P.J. Davis, C.J. Brinker, D.M. Smith and R.A. Assink, Journal of Non-Crystalline

Solids; R. Deshpande, D.W. Hua, C.J. Brinker, and D.M. Smith, Journal of Non-Crystalline Solids). In addition to metal oxide gels such as silica, aerogels may be made from wet precursor gels, which contain both inorganic and organic components, or from organic gels. For the composite gels, the organic and inorganic phases may be mixed on different length scales such that the organic component resides solely on the internal pore surface, is incorporated into the spanning gel structure, or forms a separate (from the inorganic phase) gel structure.

The conversion of the wet gel to a dried aerogel or xerogel requires the removal of large quantities of solvent. As solvent is removed, the gel tends to shrink as a result of capillary pressure. The capillary pressure Pc generated during drying is related to the pore fluid surface tension, $_{LV}$, and contact angle, θ, between the fluid meniscus and pore wall as follows,

$$P_c = -(2 \quad {}_{LV}\cos\theta)/r \qquad (1)$$

where r is the pore radius. For submicron capillaries, such as in silica gels, very large stresses are developed during drying. Aerogel synthesis involves the reduction of capillary pressure by lowering the surface tension, $_{LV}$, to avoid shrinkage of the wet gel during drying.

Aerogels are not new materials. They were first reported by Kistler almost 60 years ago (S.S. Kistler, Nature, 127 (1931) 741). However, recent advances in sol-gel processing technology along with increasing environmental concern have regenerated interest in energy conservation and alternate thermal insulation applications. The most common method of making aerogels involves

directly removing the pore fluid above its critical point (for ethanol T_c=243 °C, P_c=-63 bar). The critical point is a chemical-specific point on the pressure-temperature phase diagram and at temperature and pressure above the critical point values, a liquid and gas cannot coexist but rather, a supercritical fluid will. This avoids liquid-vapor menisci and thus, capillary stresses during drying and essentially preserves the wet gel structure. An alternate low temperature method involves replacing the pore fluid with liquid CO_2 and then removing CO_2 above its critical point (T_c=31 °C, P_c=73 bar). All of these prior approaches require high pressure supercritical processing to reduce shrinkage.

Although aerogels exhibit very unique properties, they suffer from several drawbacks for commercial applications. An important disadvantage is their high processing cost because of the need for high pressures associated with supercritical drying of monoliths which require large autoclaves. For the high temperature process significant chemical and physical changes in gel structure can occur as a result of the greatly accelerated rates of aging and changes in the equilibrium behavior of various reactions whereas the low temperature carbon dioxide exchange process is limited to certain pore fluids, since they must be miscible in liquid CO_2.

Disclosure of the Invention

This invention involves the production of a material which has the properties of a supercritically dried aerogel but with a non-supercritical process. By treating either inorganic metal oxide gels of the general formula

M_xO_y such as silica (SiO_2) and alumina (Al_2O_3), composite inorganic-organic gels of the general formula $R_xM_yO_z$, or organic gels, in the wet state before drying with surface modification agents or compounds of the formula R_xMX_y where R are organic groups such as CH_3, C_2H_5, etc. and X is a halogen, usually Cl, so that significant changes in the subsequent drying of the gels at non-supercritical pressures are obtained which leads to greatly reduced shrinkage during drying.

The presence of the organic groups on the internal surface of the pores and the proper selection of the final solvent from which the gel is dried results in a contact angle of the fluid in the pore of near 90°. This reduces the capillary pressure to near zero; see Equation (1). Thus, in contrast to high pressure supercritical drying which manipulates the surface tension of the pore fluid to lower capillary pressure during drying, the arrangement of this invention changes the contact angle to lower capillary pressure. The process consists of a series of aging, washing, and/or surface modification steps which are undertaken upon a wet gel before drying. In one embodiment of the invention, water in the water/alcohol mixture initially contained in the wet gel is removed by solvent exchange with either a protic (i.e., alcohol) or aprotic (i.e., acetone) solvent to remove water. The wet gel is then placed in a mixture of the surface modifications compound (R_xMX_y) and a solvent in which it is soluble such as benzene or toluene. After reaction, the gel is again washed with a protic or aprotic solvent and the gel is dried at sub-critical pressure (e.g., vacuum to ambient to sub-

critical pressure). Sub-critical is defined as any pressure less than the critical pressure P_{crit} for the fluid. In this manner, high porosity (0.60 < porosity) and low density (density < 0.3 g/cm^3) ambiently dried gels (xerogels) are obtained with properties essentially the same as supercritically dried aerogels.

Brief Description of the Drawings

The features of this invention, and its technical advantages, can be seen from the following description of preferred embodiments, together with the claims and the accompanying drawings, in which:

Figure 1a and 1b are schematic diagrams of fluid contained in a pore; depending upon the fluid and the surface modifications of the pore wall 1, the degree of wetting changes which causes a significant change in the meniscus shape 2 of the fluid 3 and hence, magnitude of capillary pressure;

Figure 2 is a graph depicting variation of pore volume with final pore fluid surface tension for conventional high temperature (ethanol) and low temperature (carbon dioxide) supercritically-dried aerogels, for conventional xerogels dried from pore fluids of different surface tensions, and the ambient pressure, surface modified gels processed in accordance with an embodiment of the invention;

Figure 3 is a graph showing a comparison of the pore size distributions obtained for dried gels processed using the surface modification, ambient pressure processing in accordance with the invention and xerogels which were not surface modified and dried from different solvents;

Figure 4 is a graph showing a change in

sample weight and sample length during drying for surface modified, ambient pressure gel processed in accordance with the invention, illustrating the initial shrinkage followed by expansion of the gel during the final stages of drying;

Figure 5 is a graph showing hexane imbibition into dried gels with the same pore size; the much slower rate of imbibition for the surface modified gel demonstrates the lower capillary pressure and contact angle closer to 90°; and

Figure 6 is a graph showing water intrusion illustrating the hydrophobic nature of surface modified gels, described in Example 1, in accordance with the invention.

Best Modes for Carrying out the Invention

In accordance with the invention inorganic metal oxide gels such as silica (SiO_2) and alumina (Al_2O_3) and of the general formula M_xO_y or inorganic-organic composite gels of the formula $R_xM_yO_z$ or organic gels are treated in the wet state before drying with a suitable surface modification compound. Such compound may take the form R_xMX_y where R are organic groups such as CH_3, C_2H_5, etc. and X is a halogen, usually Cl. In accordance with the invention, the surface modification compound greatly reduces shrinkage during drying. As described earlier, capillary pressure causes the gel to collapse during drying.

By decreasing the magnitude of the capillary pressure, less shrinkage is obtained during drying. Because the surface area of wet gels is very high (10-2000 m^2/g), a significant fraction of the atoms in the gel will be surface species. For a metal oxide gel, the surface will be terminated with either hydroxyl (OH) or alkoxy (OR) groups. In

prior art drying processes, these surface groups react to produce MOM bonds via water producing (MOH + MOH <-> MOM + H_2O) or alcohol-producing (MOH + MOR <-> MOM + ROH) condensation reactions. These MOM bonds thus retain the structure of the collapsed wet gel and, disadvantageously, do not allow the gel to expand after the capillary pressure is released, i.e., dried. In accordance with the invention by capping these MOH and MOR surface groups with surface modification compounds of the form R_xMX_y, the surface becomes covered with unreactive MR_x groups. Advantageously, the unreactive MR_x groups increase the contact angle of the fluid meniscus in the pores of the wet gel and prevent condensation reaction during drying. While surface modifications groups have previously been employed to modify the surface properties of material to make them hydrophobic, such groups, as employed in this invention for a much different purpose, are used to modify the contact angle of the fluid meniscus in the pores during drying to minimize shrinkage of the gel.

The process used in accordance with the invention consists of a surface modification step which is undertaken upon a wet gel before drying. The wet gel may be produced via hydrolysis and condensation of metal alkoxides, gelling of particular or colloidal metal oxides, gelation of organic precursors, or a combination of these approaches. A series of aging steps to increase wet gel strength and washing steps to remove water from the wet gel, since water reacts with the surface modification compound, may be used before the surface modification step.

If water is contained in the wet gel, it

may be removed by solvent exchange with either a protic (i.e., alcohol) or aprotic (i.e., acetone, hexane) solvent. The wet gel is then placed in a mixture of the surface modification compound (R_xMX_y) and a solvent in which the surface modification compound is soluble and which is miscible with the solvent in the gel. A wide range of solvents such as benzene, toluene, and hexane may be used. The surface modification compound reacts with hydroxyl groups on the surface (e.g., $R_3MCl + MOH \rightarrow MOMR_3 + HCl$). After the reaction is completed, the gel is again washed with a protic or aprotic solvent and the gel is dried at pressures less than the critical point (vacuum to sub-critical pressure) and typically at ambient temperature. As a consequence of the surface modification, the wetting angle θ is much larger and the meniscus shape is flatter as shown in Figure 1b. This results in significantly lower capillary pressure during drying than would exist for a gel not modified in accordance with the invention. As a result of the lower capillary pressure, little linear shrinkage occurs during drying. The small degree of shrinkage (less than 5% of the sample length) results in low density, high porosity dried gels. For a gel not modified in accordance with the invention, the linear shrinkage under the same drying conditions would exceed 30%. In this manner, in accordance with the invention, high porosity ($0.60 < \text{porosity} < 0.95$), low density ($0.1 < \text{density} < 0.3$ g/cm^3) dried gels (xerogels) are obtained with properties essentially the same as supercritically-dried aerogels. Specific processes and the resultant dried gel properties in accordance with embodiments of the

invention are illustrated in the following Examples.

Example 1 Surface Modification and Drying of Alkoxide-Derived Silica Gel:
Complete Washing Before Modification

Silica gel via two-step base catalysis of TEOS (B2 gel)

Step 1: TEOS stock solution preparation tetraethylorthosilicate (TEOS), ethanol, water, and HCL in the molar ratio 1:3:1:0.0007 under constant reflux for 1.5 hours at 333 K:

61 ml TEOS
61 ml Ethanol
4.87 ml Water
0.2 ml 1M HCL

Step 2: 10 ml of TEOS stock solution was gelled by adding 1 ml of 0.05 M NH_4OH. Gelation occurred at approximately 1.5 hours at 310 K in glass bottles.

Aging and Washing

1) After gelation the sample was aged 22 hours at 310 K.
2) Samples were washed 5 times with excess (approx. 10 times the volume of gel samples) absolute ethanol at 310 K. Each washing cycle was 24 hours each.

Surface Modification and Washing

1) Surface modification using trimethylchlorosilane (TMCS) where R is CH_3, x is 3, M is Si, X is Cl, and y is 1. Surface modification of the ethanol washed samples was carried out by shaking these samples with an excess amount of 10

volume % TMCS in benzene for 48 hours at room temperature.

2) Unreacted surface modification compound was removed by washing the gels with an excess amount of an aprotic solvent. This was achieved by shaking the samples with the solvent for 48 hours at room temperature. Different solvents used at this step were as follows:

ID	Aprotic Solvent	Surface Tension dyne/cm
A	THF	23.1
B	Acetone	23.7
C	Benzene	29
D	Acetonitrile	29.3
E	1, 4 Dioxane	33.6

Drying

Excess aprotic solvent was drained and samples were dried at ambient pressure for 24 hours at room temperature followed by at 323 K and 373 K for 24 hours each.

Results

ID	Surface Tension (dyne/cm)	Surface Area (m^2/g)	Pore Vol. (cm^3/g)	Porosity	Av. Pore Radius (nm)
A	23.1	869.4	2.259	0.82	5.95
B	23.7	843.7	2.23	0.82	5.28
C	29.0	850.3	2.23	0.82	5.24
D	29.3	837.1	2.25	0.82	5.37
E	33.6	826.9	2.62	0.84	6.33

<u>Example 2: Surface Modification and Drying of Alkoxide-Derived-Silica Gel: Drying from Acetone</u>

Wet Silica gel via two-step base catalysis of TEOS (B2 gel)

Step 1: TEOS stock solution preparation tetraethylorthosilicate (TEOS), ethanol, water, and HCI in the molar ratio

1:3:1:0.0007 under constant reflux for 1.5 hours at 333K:

61 ml TEOS

61 ml Ethanol

4.87 ml Water

0.2 ml 1M HCl.

Step 2: 10 ml of TEOS stock solution was gelled by adding 1 ml of 0.05 M NH_4OH. Gelation occurred at approximately 1.5 hours at 310 K in plastic cylindrical molds.

Aging and Washing

1) After gelation the sample was aged 22 hours at 310 K, followed by 24 hour aging at 323K.

2) The sample was washed once with excess (approx. 10 times the volume of gel samples) acetone at 310 K. Each washing cycle was 24 hours.

Surface Modification and Washing

1) Surface modification using trimethylchlorosilane (TMCS) where R is CH_3, x is 3, M is Si, X is Cl, and y is 1. Surface modification of acetone washed sample was carried out by shaking these samples with excess amount of 10 volume% TMCS in benzene for 48 hours at room temperature.

2) Unreacted surface modification compound was removed by washing the gel with an excess amount of an aprotic solvent. This was achieved by shaking the samples with the solvent for 48 hours at room temperature. One solvent used at this step was:

Aprotic Solvent: THF, Surface Tension (dyne/cm):

samples was carried out by shaking these samples with an excess amount of 10 volume% TMCS in benzene for 48 hours at room temperature.

1b) Surface modification using trichloromethylsilane (TCMS) where R is CH_3, x is 1, M is Si, X is Cl, and y is 3. Modification of acetone washed samples was carried out by shaking these samples with an excess amount of 10 volume% TCMS in benzene for 48 hours at room temperature.

2) Unreacted surface modification compound was removed by washing the gels with excess amounts of an aprotic solvent. This was achieved by shaking the samples with the solvents for 48 hours at room temperature. The aprotic solvent used at this stage was n-hexane.

Drying

1) Excess aprotic solvent was drained and the samples were dried at ambient pressure for 24 hours at room temperature followed by at 323 K and 373 K for 24 hours each.

Results

Porosity = 0.8

<u>Example 4: Organic-Inorganic Composite Gel by the Substitution of a Gel Structure Modifier for Tetraethyl Orthosilicate: Organic Phase on Pore Surface</u>

Preparation of wet gel by two-step base-catalysis of TEOS and MTEOS

Step 1: TEOS stock solution was modified by the

partial substitution of methyltriethoxysilane (MTEOS) for tetraethylorthosilicate (TEOS). Two stock solutions were prepared, regular TEOS stock solution and 50/50 TEOS/MTEOS. Preparation of the MTEOS stock solution consists of using a ratio of TEOS/MTEOS equal to 0.5 based on the amount of Si. TEOS, MTEOS, Ethanol, water, and HCl in the molar ratios of 1:1:8:2:0.0014 were refluxed for 4 hours at 333 K:

30.5 ml TEOS
27.3 ml MTEOS
64.2 ml Ethanol
4.87 ml Water
0.2 ml 1 M HCl

Step 2: Different percentages of the MTEOS gels were prepared by mixing different ratios of the TEOS stock solution and MTEOS stock solution.

% Modified Ester	TEOS stock	50/50 Stock
10	8	2
20	6	4
30	4	6
40	2	8
50	0	10

Step 3: 10 ml of the modified stock solution was gelled by adding 1 ml of 0.5 M NH_4OH. Gelation occurred in the range of 30 minutes to 10 hours in plastic cylinders at 310 K. Gelation time increased with increasing modification with MTEOS.

Aging and Washing

1) After the samples were gelled at 310 K they were aged at 323 K for 24 hours.

2) The samples were washed three times in three hours with excess absolute ethanol at 323 K, followed by two washings with hexane in two hours. After the second hexane wash, the samples were kept at 323 K for 24 hours in hexane.

Surface Modification and Washing

1) Surface modification was carried out by immersing the wet gel in 5 vol. % trimethylchlorosilane in hexane for 24 hours at 323 K.

2) Unreacted TMCS was removed after 24 hours by washing the gel an additional two times with hexane.

Drying

Excess hexane was drained and the gel was dried at 310 K, 323 K, and 413 K for 24 hours each.

Results

% Modified Ester	Bulk Density (g/cc)
20	0.18
50	0.21

Example 5: Organic-Inorganic Composite Gel by the Substitution of a Gel Structure Modifier for Tetraethyl Orthosilicate: Organic Phase Incorporated in Gel-Bridging Structure

Preparation of wet gel by two-step base catalysis of TEOS and BTMSE

Step 1: TEOS stock solution was modified by the partial substitution of 1,2-bis(trimethoxysilyl)ethane (BTMSE) for tetraethylorthosilicate (TEOS). Two stock solutions were prepared, 50/50 BTMSE stock solution consists of using a ratio of TEOS/BTMSE equal to 0.5 based on

the amount of Si. TEOS, BTMSE, ethanol, water, and HCl in the molar ratios of 1:0.5:6:2:0.0014 were refluxed for 4 hours at 333 K. The 100% BTMSE was calculated using the same molar ratio of Si as in normal 15% TEOS stock solution. BTMSE, ethanol, water, and HCl in the molar ratios of 1:6:2:0.0014 were refluxed for 4 hours at 333K:

50/50 BTMSE/TEOS	100 BTMSE
30.50 ml TEOS	34.28 ml BTMSE
17.13 ml BTMSE	87.72 ml Ethanol
74.37 ml Ethanol	4.87 ml Water
4.87 ml Water	0.2 ml 1 M HCl
0.2 ml 1 M HCl	

Step 2: Different percentages of the BTMSE gels were prepared by mixing different ratios of the 50/50 TEOS/BTMSE stock solution and BTMSE stock solution.

% Modified Ester	50/50 Stock	BTMSE stock
50	10	0
60	8	2
70	6	4
80	4	6
90	2	8
100	0	10

Step 3: 10 ml of the modified stock solution were gelled by adding 1 ml of 0.5 M NH_4OH. Gelation occurred in the range of one hour to 12 hours in plastic cylinders. Gelation time increased with increasing modification with BTMSE.

Aging and Washing

1) After the samples were gelled at 310 K they were aged at 323 K for 24 hours.

2) The samples were washed three times in three hours with excess absolute ethanol at 323 K, followed by two washings of hexane in two hours. After the second hexane wash, the samples were kept at 323 K for 24 hours in hexane.

Surface Modification and Washing

1) Surface modification was carried out by immersing the gel in 5 vol. % trimethylchlorosilane in hexane for 24 hours at 323 K.

2) Unreacted TMCS was removed after 24 hours by washing the gel an additional two times with hexane.

Drying

Excess hexane was drained and the gel was dried at 310 K, 323 K, and 413 K for 24 hours each.

Results

% Modified Ester	Bulk Density (g/cc)
50	0.26
60	0.27
70	0.27
80	0.29
90	0.32
100	0.32

The dried gels were characterized by conventional porous material analysis techniques including BET analysis of nitrogen adsorption isotherms at 77 K (surface area), analysis of the desorption branch of the nitrogen isotherm (pore size distribution), the difference between the bulk and skeletal densities and/or the total volume of nitrogen condensed at high relative pressure (total pore volume), and the drying characteristics

(weight loss and sample length change). The pore volume (V_p, the total pore volume per mass of the dried gel) is related to the porosity (ε, the fraction of the total material volume which is porous) by $\varepsilon = V_p/(V_p + 1/\rho_t)$ where ρ_t is the skeletal density of the solid matrix which is usually measured via helium displacement. For silica gels, ρ_t is approximately 2 g/cm^3 and thus, a pore volume of 2 cm^3/g corresponds to a solid which is 80% air and a pore volume of 4.5 cm^3/g corresponds to a solid which is 90% air.

The pore volume for a number of silica gels made using the B2 silica gel recipe described above are shown in Figure 2 and were: 1) surface modified and dried from a variety of solvents at ambient pressure: Examples 1) and 2) dried from solvents without surface modification at ambient pressure (conventional xerogel process), 3) supercritically dried without surface modification at high temperature from ethanol (conventional aerogel process), and 4) supercritically dried without surface modification at low temperature from carbon dioxide (conventional aerogel process). The pore volumes for the surface modified gels are independent of surface tension and essentially equal to the two different aerogel samples. The pore size distribution for several of the surface modified gels in accordance with the invention is presented in Figure 3 and shows the same lack of dependence on surface tension. For comparison, two unmodified gels are included to show the collapse (i.e., decrease in pore size) that would normally occur during conventional drying. Normally, as a gel is dried, it undergoes a monotonic decrease in size.

However, by capping the surface sites in accordance with the invention, the invention process actually results in an expansion during the final stages of drying as shown in Figure 4. In carrying out processing accordance with the invention, the degree of this shrinkage and subsequent recovery in sample size is a function of the surface tension of the fluid and fluid-pore wall contact angle. After surface modification, the gels are hydrophobic as compared to conventional gels which are hydrophilic. This is illustrated in Figure 5. A significant external pressure is required to force water into the pores of the surface modified, ambient pressure gels. For a conventional unmodified aerogel or xerogel, water would rapidly wick into the gel at ambient pressure destroying its mechanical and insulating properties.

In order to demonstrate that the capillary pressure in surface modified gels made via this process have a lower capillary pressure during drying, imbibition experiments were performed on both modified and unmodified samples. In this experiment, a dried gel is brought into contact with the fluid. The fluid wicks into the dried gel due to capillary pressure. From the rate of uptake, the contact angle is determined. Figure 6 is a plot of imbibition uptake curves for n-hexane. If the contact angle for both samples was the same, the slopes of the curves would match. The final height is different for the samples because different sample lengths were employed. Contact angles for four different fluids and both modified and not modified gels are shown in Table 1. The contact angle is consistently nearer to 90°

(lower capillary pressure) for the surface modified gels.

Table 1: Contact angles for surface modified gels dried at ambient pressure and unmodified gels dried using supercritical processing

Fluid	Surface Modified (ambient pressure)	Not Surface Modified (supercritical)
ethanol	76.7°, 78.4°	30.3°, 35.1°
acetone	79.3°, 77.2°	29.1°, 37.2°
hexane	89.6°, 82.7°	41.3°, 48.4°
1, 4-dioxane	81.1°	66.4°

Accordingly, it is seen that the invention advantageously provides an extremely low density finely pored gel through an inexpensive process not requiring high pressure, having beneficial and useful insulating and other properties.

Claims

1. A method of producing a dried xerogel of porosity greater than about 0.6, characterized by the following steps:

a) providing a gel in the wet state, the wet gel having a pore fluid contact angle 0 and a substantial number of its atoms which are surface species;

b) reacting the wet gel with a surface modification agent so as to cause replacement of a substantial number of the surface species with a different species which different species substantially increase the pore fluid contact angle 0, and

c) drying the wet gel at at least one pressure selected to be within the range from vacuum to sub-critical.

2. The method of claim 1, characterized in that the wet gel contains water and in that the step a) includes the further step of removing substantially all of the water from the wet gel, thereby leaving the wet gel in the wet state so as to contain substantially less water.

3. The method of claim 1, characterized in that the step a) further includes aging the wet gel at an elevated temperature for a predetermined period.

4. The method of claim 3, characterized in that the elevated temperature is within the range of ambient to about the boiling point of the fluid in the wet gel.

5. The method of claim 3, characterized in that the step a) further includes, after aging, washing the wet gel with a solvent selected from the group of a protic solvent and an aprotic

solvent.

6. The method of claim 1, characterized in that the step a) includes aging the wet gel at a temperature up to the boiling point of the fluid in the wet gel and washing the wet gel in a solvent selected from the group of a protic solvent and an aprotic solvent to remove substantially all of the water from the wet gel.

7. The method of claim 1, characterized in that the step b) further includes organosilylating the wet gel in a selected solvent.

8. The method of claim 7, characterized in that the selected solvent is an organic solvent.

9. The method of claim 1, characterized in that the step of reacting further includes removing unreacted surface modification agent with a solvent selected from the group of protic solvent and an aprotic solvent.

10. The method of claim 1, characterized in that the gel is a metal oxide gel prepared from a solution of tetraethylorthosilicate (TEOS).

11. The method of claim 1, characterized in that the gel is a metal oxide gel prepared from silica selected from the group of a colloidal silica and a particulate silica.

12. The method of claim 1, characterized in that the gel is a metal oxide gel prepared from a material selected from the group at an alkoxide and a particulate gel and a combination of alkoxide and particulate gel.

13. The method of claim 1, characterized in that the step of drying is performed in a range of pressures between vacuum and sub-critical and in a range of temperatures between ambient and the boiling point of the fluid in the wet gel, until

the gel does not undergo any further weight loss.

AMENDED CLAIMS

[received by the International Bureau on 18 October 1994 (18.10.94); original claims 2 and 5 deleted; remaining claims amended (2 pages)]

1. A method of producing a xerogel of porosity greater than about 0.6, characterized by the following steps:

a) providing a gel in the wet state containing water, the wet gel having a pore fluid contact angle Θ and a substantial number of its atoms which are surface species;

b) exchanging substantially all of the water contained in the wet gel with a protic or aprotic solvent;

c) reacting the wet gel with a surface modification agent R_xMX_y, wherein R is an organic group, M is selected from the group consisting of Si and Al, and X is halogen, to cause replacement of a substantial number of surface species with a different species which substantially increase the pore fluid contact angle Θ; and

d) drying the wet gel at at least one pressure selected to be within the range from vacuum to sub-critical.

3. The method of claim 1, characterized by a further step of aging the wet gel at an elevated temperature for a predetermined period before the step of exchanging.

4. The method of claim 3, characterized in that the elevated temperature is within the range of ambient to about the boiling point of the water in the wet gel.

6. The method of claim 1, characterized by a further step of aging the wet gel at a temperature up to the boiling point of the solvent after the step of exchanging.

7. The method of claim 1, characterized in that in the step c) the wet gel is reacted with an organosilane in a selected solvent.

8. The method of claim 7, characterized in that the selected solvent is an organic solvent.

9. The method of claim 1, characterized in that the step of reacting further includes removing unreacted surface

modification agent with a protic solvent or an aprotic solvent.

10. The method of claim 1, characterized in that the step a) includes the step of preparing the gel as a metal oxide gel from a solution of tetraethylorthosilicate (TEOS).

11. The method of claim 1, characterized in that the step a) includes the step of preparing the wet gel as a metal oxide gel from a colloidal silica or a particulate silica.

12. The method of claim 1, characterized in that the step a) includes the step of preparing the wet gel as a metal oxide gel from an alkoxide, a particulate gel or a combination of an alkoxide and particulate gel.

13. The method of claim 1, characterized in that the step of drying is performed in a range of pressures between vacuum and sub-critical and in a range of temperatures between ambient and the boiling point of the solvent in the wet gel, until the gel does not undergo any further weight loss.

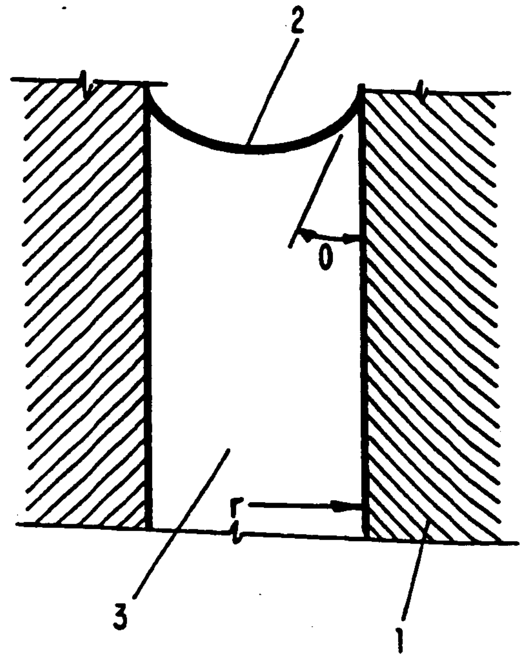


FIG-1a

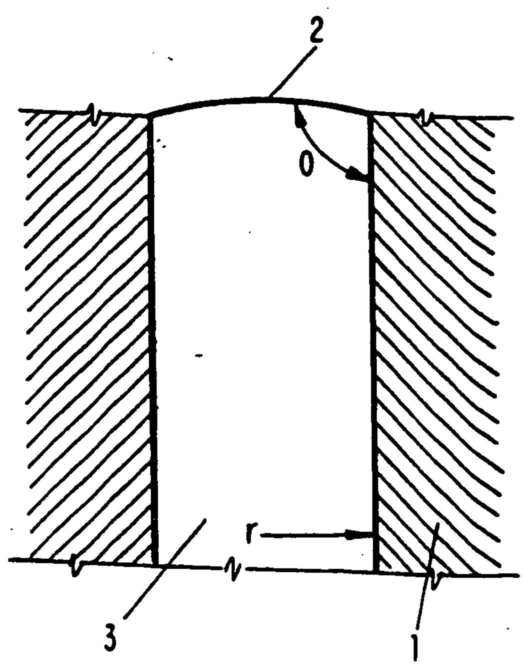


FIG-1b

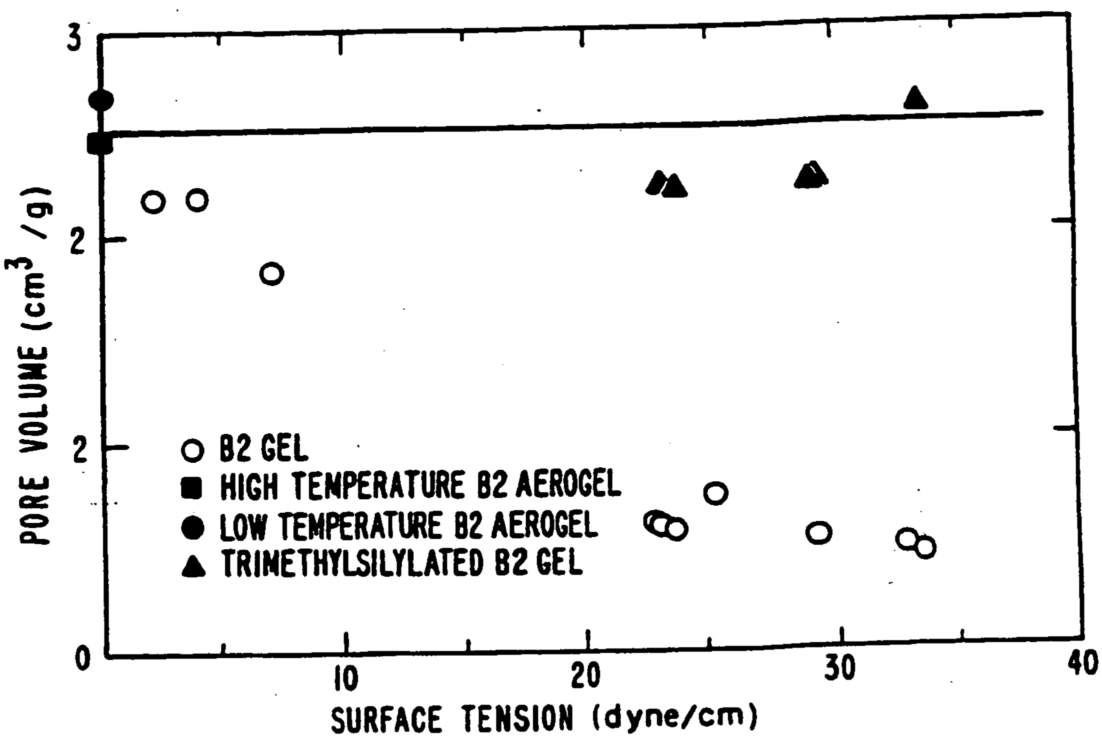

PORE VOLUME (cm³ /g)
SURFACE TENSION (dyne/cm)
B2 GEL
HIGH TEMPERATURE B2 AEROGEL
LOW TEMPERATURE B2 AEROGEL
TRIMETHYLSILYLATED B2 GEL
0
2
2
3
10
20
30
40

FIG — 2

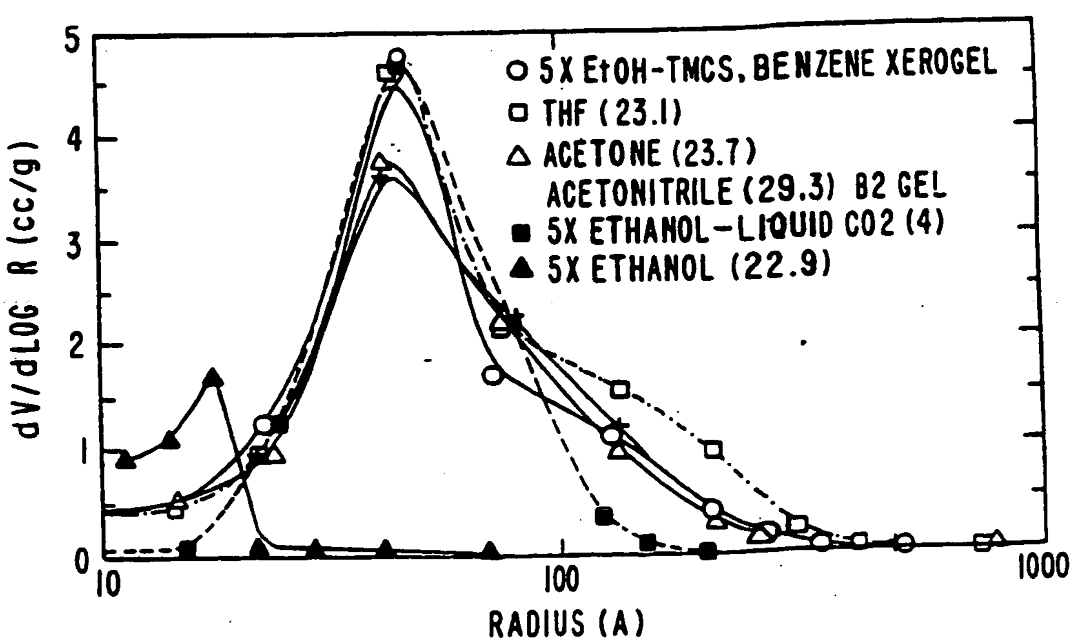
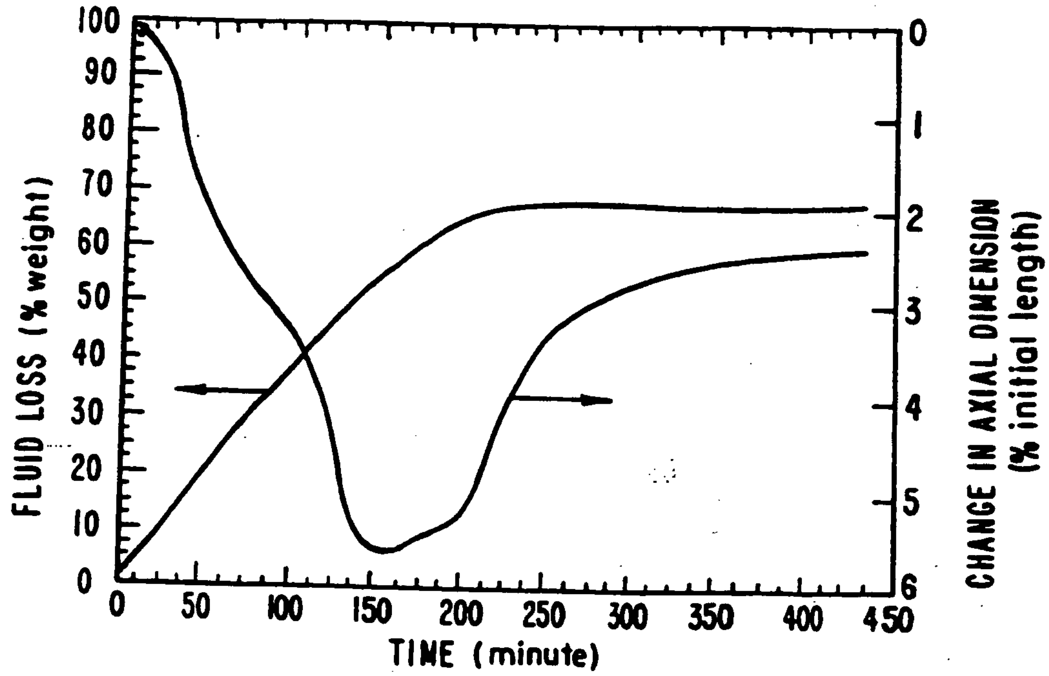
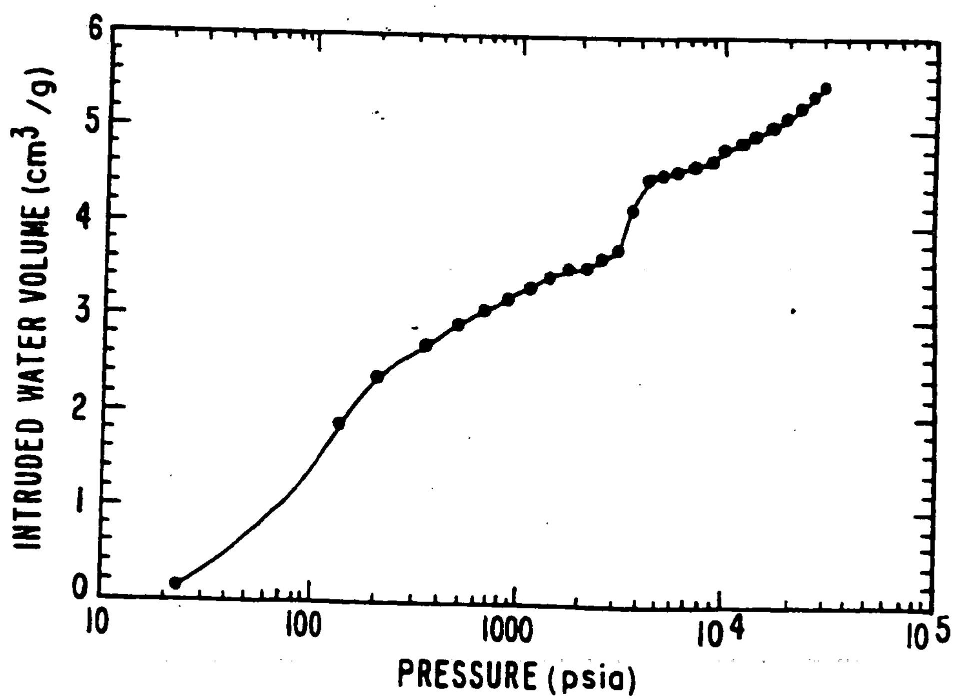

dV/dLOG R (cc/g)
RADIUS (A)
5X EtOH-TMCS, BENZENE XEROGEL
THF (23.1)
ACETONE (23.7)
ACETONITRILE (29.3) B2 GEL
5X ETHANOL-LIQUID CO2 (4)
5X ETHANOL (22.9)
0
1
2
3
4
5
10
100
1000

FIG — 3


100
90
80
70
60
50
40
30
20
10
0
FLUID LOSS (% weight)
0
1
2
3
4
5
6
CHANGE IN AXIAL DIMENSION (% initial length)
0
50
100
150
200
250
300
350
400
450
TIME (minute)

FIG—4


6
5
4
3
2
1
0
INTRUDED WATER VOLUME (cm^3/g)
10
100
1000
10^4
10^5
PRESSURE (psia)

FIG—5

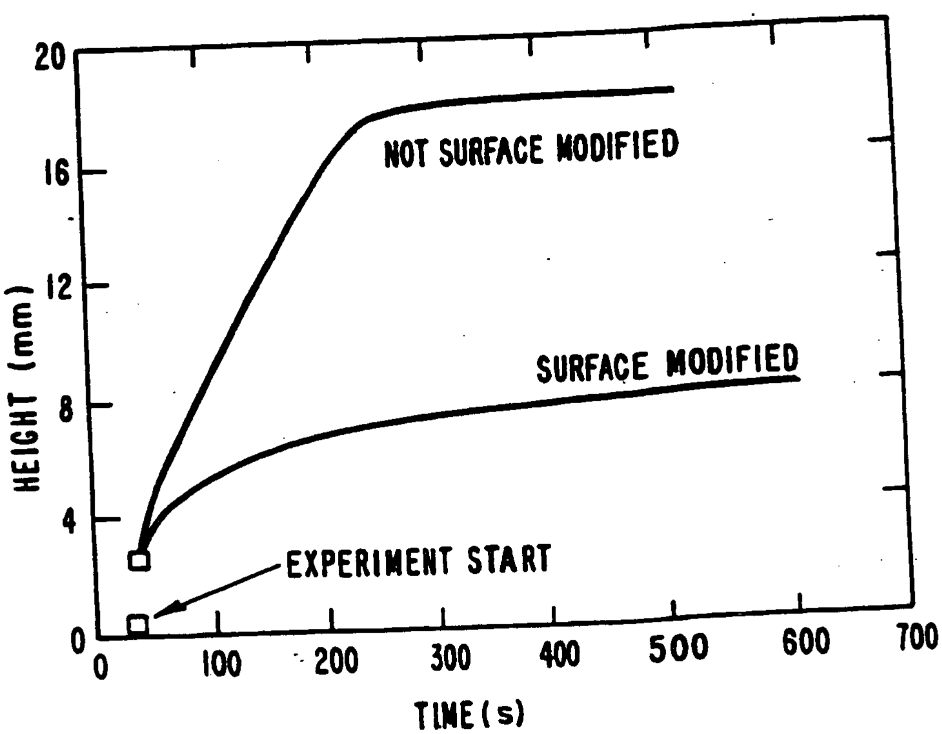

20
16
12
8
4
0
HEIGHT (mm)
NOT SURFACE MODIFIED
SURFACE MODIFIED
EXPERIMENT START
0
100
200
300
400
500
600
700
TIME (s)

FIG — 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/US94/05105

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) Please See Extra Sheet.
US CL 252/62.315.2.315.6.315.7; 427/220; 501/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. 252/62.315.2.315.6.315.7; 427/220; 501/12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,963,627 (COTTRELL) 15 JUNE 1976, SEE EXAMPLES; AND COL. 2, LINE 21-COL. 5, LINE 39).	1-13
Y	US, A, 4,316,807 (MC DANIEL ET AL) 23 FEBRUARY 1982, SEE EX.'S VII & I; AND COL. 4, LINE 7, COL. 5, LINE 5.	1-13
Y	US, A, 2,765,242 (ALEXANDER ET AL) 02 OCTOBER 1956, SEE EX. 5	5,6
Y	US, A, 2,993,809 (BUECHE ET AL.) 25 JULY 1961, SEE COL. 2, LINES 15-26.	7-9
Y	US, A, 4,017,528 (UNGER ET AL.) 12 APRIL 1977, SEE EX. 1; AND COL. 5, LINES 23 & 24.	10

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be part of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 12 AUGUST 1994	Date of mailing of the international search report AUG 29 1994
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer Diane Goodwin for RICHARD D. LOVERING Telephone No. (703) 308-0443

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/05105

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 2,978,298 (WETZEL ET AL.) 04 APRIL 1961	1-13
A	US, A, 3,210,273 (TAULLI) 05 OCTOBER 1965	1-13
A	US, A, 3,346,507 (TAULLI) 10 OCTOBER 1967	1-13
A	US, A, 3,803,046 (WINYALL ET AL) 09 APRIL 1974	1-13
A	US, A, 4,447,345 (KUMMERMEHR ET AL.) 08 MAY 1984	1-13

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/05105

A. CLASSIFICATION OF SUBJECT MATTER:
IPC (5):

B01J 13/00; B05D 7/00; C03C 17/30; E04B 1/74